



An emerging platform for electrocatalysis: perovskite exsolution

Keke Huang

Published online: 7 November 2016

© Science China Press and Springer-Verlag Berlin Heidelberg 2016

The design of cost-effective, highly active, stable electrocatalysts for oxygen reduction reaction (ORR) and oxygen evolution reaction (OER) is a critical element in the development of a new generation of energy technologies (e.g., fuel cells, metal-air batteries) because the ORR and OER are inherently sluggish and require large over-potentials to drive a complex four-electron process [1]. So far, precious metals platinum (Pt) and its alloys are the most active electrocatalysts for ORR but have poor activity for OER. Oppositely, IrO₂ is the most active for OER but not effective for ORR. To date, nitrogen-doped carbon has shown remarkable ORR activity, but its OER is more challenging due to the rapid oxidation of carbon at high potentials [2]. For the chemists, tailoring and optimizing of functional materials are an urgent topic.

Surfaces are a key platform for many processes of catalysis and energy conversion. Understanding and controlling electronic structure and geometric environment of their surfaces or interfaces are key factors in optimizing renewable energy and catalysis [3]. Surfaces decorated with nanoparticles have been demonstrated in many fields of catalysis. These structures are usually obtained by conventional deposition techniques, such as pulsed laser deposition and chemical impregnation. These approaches offer limited control over the size, distribution and anchorage of deposited species and may be time-consuming and costly. Recently, Irvine and co-workers [4] demonstrated that growing nanosize phases from non-stoichiometry perovskites can be achieved by means of an exsolution process under a

reductive environment (Fig. 1). The non-stoichiometry facilitates a change in equilibrium position to make particle exsolute more dynamic with obtaining compositionally diverse nanoparticles [4]. In fact, back to more than ten years ago, the self-regeneration Pd-perovskite catalysts has been discovered for automotive emissions control. The smart catalyst is cycled between oxidative and reductive atmospheres, and Pd may reversibly move into and out of the perovskite lattice [6]. Subsequently, this self-regenerating function was realized in Pt and Rh-based perovskite catalysts, as well as in Pd [7].

The chemical exsolving technique has been adopted for successful fabrication of silver modified Sr_{0.95}Nb_{0.1}Co_{0.9}O₃ as a highly active and durable electrocatalyst for ORR, which makes the new composite material a highly promising cathode for low-temperature solid oxide fuel cells [8]. In contrast to metal particles formed on an oxide support by physical or chemical deposition, the exsolved particles show enhanced stability and a significant decrease in the propensity for hydrocarbon coking due to partly embedded in the surface of a parent perovskite. This study is critical to future design of exsolution-based perovskite materials for catalytic and other functionalities [5].

It is well known that pure perovskites (ABO₃) are promising electrocatalytic materials due to high versatility in their electronic structure. But, the true catalytic properties of many perovskites might have been underestimated because native perovskite surfaces are preferentially A-site (rich) terminated to the detriment of the B-sites of catalytically active cations [4]. New techniques have been developed to exsolve the B-sites from parent perovskite lattice by external fields and chemically selective exsolution [9]. It shows that perovskite-type oxides could work as the most appropriate host materials to form socked metal–semiconductor heterostructures that leads to superior catalytic activity while

K. Huang (✉)

State Key Laboratory of Inorganic Synthesis and Preparative Chemistry, College of Chemistry, Jilin University, Changchun 130012, China
e-mail: kkhuang@jlu.edu.cn

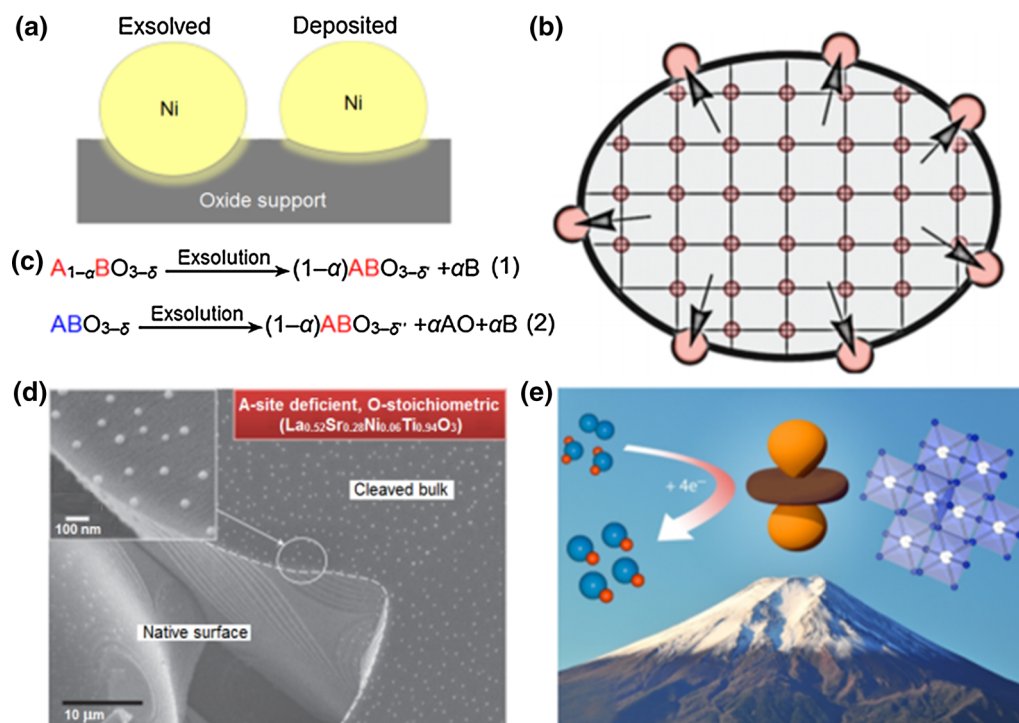


Fig. 1 (Color online) Exsolution in perovskite structure oxides as a new platform for electrocatalyst design. **a** Comparison of exsolved with deposited nanoparticles on oxide support. Reprinted with permission from Ref. [4], Copyright 2013 Nature Publishing Group. **b** The exsolution process of nanoparticles from perovskite lattice; **c** defect-induced B-site exsolution reaction in perovskite; **d** monodispersed Ni-nanoparticles on A-site-deficient perovskite. Reprinted with permission from Ref. [5], Copyright 2015 Nature Publishing Group. **e** Electrocatalytic design by tunable orbital and structure (<http://news.mit.edu/2011/battery-principle-0613>)

keeping the stability of parent perovskite. The formation of metal particles supported on oxide surfaces promotes numerous global chemical industry reactions and processes towards clean energy technologies.

In summary, exsolution in perovskite structure oxides provides a platform for understanding and controlling electrochemical processes occurring at the interface in optimizing electrocatalysts. Especially, recent reports show that applied electrical potentials can significantly enhance exsolution in perovskite system to generate more or less instantly rich nanostructures with outstanding activity and stability [10]. By utilizing the concept of developing exsolution, perovskite structure oxides could be employed as a versatile material bank for unlimited heterogeneous surfaces catalyst design, which will surely promote the design and preparation of new metastable materials and the delicate support for single-atom catalysts.

Acknowledgments This work was supported by the National Natural Science Foundation of China (21427802 and 21671076).

References

- Zhu YL, Zhou W, Yu J et al (2016) Enhancing electrocatalytic activity of perovskite oxides by tuning cation deficiency for oxygen reduction and evolution reactions. *Chem Mater* 28:1691–1697
- Gupta S, Kellogg W, Xu H et al (2016) Bifunctional perovskite oxide catalysts for oxygen reduction and evolution in alkaline media. *Chem Asian J* 11:10–21
- Huang KK, Chu XF, Yuan L et al (2014) Engineering the surface of perovskite $\text{La}_{0.5}\text{Sr}_{0.5}\text{MnO}_3$ for catalytic activity of CO oxidation. *Chem Commun* 50:9200–9203
- Dragos N, George T, David NM et al (2013) In situ growth of nanoparticles through control of non-stoichiometry. *Nat Chem* 5:916–923
- Dragos N, Tae-Sik O, David NM et al (2015) Nano-socketed nickel particles with enhanced coking resistance grown in situ by redox exsolution. *Nat Commun* 6:8120
- Nishihata Y, Mizuki J, Akao T et al (2002) Self-regeneration of a Pd-perovskite catalyst for automotive emissions control. *Nature* 418:164–167
- Hirohisa T, Masashi T, Mary U et al (2006) Self-regenerating Rh- and Pt-based perovskite catalysts for automotive-emissions control. *Angew Chem Int Ed* 45:5998–6002
- Zhu YL, Zhou W, Ran R et al (2015) Promotion of oxygen reduction by exsolved silver nanoparticles on a perovskite scaffold for low-temperature solid oxide fuel cells. *Nano Lett* 16:512–518
- Zhang W, Zheng WT (2015) Exsolution-mimic heterogeneous surfaces: towards unlimited catalyst design. *ChemCatChem* 7:48–50
- Jae-ha M, Dragos N, David NM et al (2016) Switching on electrocatalytic activity in solid oxide cells. *Nature* 537:528–531